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Dynamics and Reactivity Patterns***

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Ionic Liquids: Radiation Chemistry, Solvation Dynamics and Reactivity Patterns

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Program Definition

Ionic liquids (ILs) are a rapidly expanding family of condensed-phase media with important applications in energy production, nuclear fuel and waste processing, improving the efficiency and safety of industrial chemical processes, and pollution prevention. ILs are generally nonvolatile, noncombustible, highly conductive, recyclable and capable of dissolving a wide variety of materials. They are finding new uses in chemical synthesis, catalysis, separations chemistry, electrochemistry and other areas. Ionic liquids have dramatically different properties compared to conventional molecular solvents, and they provide a new and unusual environment to test our theoretical understanding of charge transfer and other reactions. We are interested in how IL properties influence physical and dynamical processes that determine the stability and lifetimes of reactive intermediates and thereby affect the courses of chemical reactions and product distributions.

Successful use of ionic liquids in radiation-filled environments, where their safety advantages could be significant, requires an understanding of ionic liquid radiation chemistry. For example, characterizing the primary steps of IL radiolysis will reveal radiolytic degradation pathways and suggest ways to prevent them or mitigate their effects on the properties of the material. An understanding of ionic liquid radiation chemistry will also facilitate pulse radiolysis studies of general chemical reactivity in ILs, which will aid in the development of applications listed above. Very early in our radiolysis studies it became evident that slow solvation dynamics of the excess electron in ILs (which vary over a wide viscosity range) increases the importance of pre-solvated electron reactivity and consequently alters product distributions. Parallel studies of IL solvation phenomena using coumarin-153 dynamic Stokes shifts and polarization anisotropy decay rates are done to compare with electron solvation studies and to evaluate the influence of ILs on charge transport processes.

Methods. Picosecond pulse radiolysis studies at BNL's Laser-Electron Accelerator Facility (LEAF) are used to identify reactive species in ionic liquids and measure their solvation and reaction rates. We and our collaborators (R. Engel (Queens College, CUNY) and S. Lall-Ramnarine, (Queensborough CC, CUNY)) develop and characterize new ionic liquids specifically designed for our radiolysis and solvation dynamics studies. IL solvation and rotational dynamics are measured by TCSPC and fluorescence upconversion measurements in the laboratory of E. W. Castner at Rutgers Univ. Investigations of radical species in irradiated ILs are carried out at ANL by I. Shkrob and S. Chemerisov using EPR spectroscopy. Diffusion rates are obtained by PGSE NMR in S. Greenbaum's lab at Hunter College, CUNY and S. Chung's lab at William Patterson U. Professor Mark Kobrak of CUNY Brooklyn College performs molecular dynamics simulations of solvation processes. A collaboration with M. Dietz and coworkers at ANL is centered around the properties and radiolytic behavior of ionic liquids for nuclear separations. Collaborations with C. Reed (UC Riverside), D. Gabel (U. Bremen) and J. Davis (U. South Alabama) are aimed at characterizing the radiolytic and other properties of borated ionic liquids, which could be used to make fissile material separations processes inherently safe from criticality accidents.

Recent Progress

Pre-solvated electron reactivity and its relation to solvation dynamics in ILs. In the course of kinetic measurements on reactions of electrons with various scavengers it was found that relatively low scavenger concentrations substantially reduced the initial yield of solvated electrons. Direct scavenging of pre-solvated ("dry") electrons competes effectively with the slower electron solvation processes in ionic liquids. For example, a pyrene concentration of only 63 mM reduces the solvated electron yield to 37% of the scavenger-free value. This finding has major implications for processing of radioactive materials, where seemingly innocuous quantities of solutes may scavenge electrons very effectively. Conversely, dry electron scavenging facilitates the use of pulse radiolysis in electron transfer studies by providing a way to circumvent diffusion-limited precursor formation rates. Measurements of excess electron solvation processes and emission dynamics (Stokes shift and polarization

anisotropy decay) of solvatochromic coumarin-153 show that the reorganization dynamics of ionic liquids occur on much longer timescales (nanoseconds) than in conventional polar solvents (picoseconds). The slow solvation dynamics would also be expected to significantly alter transition state dynamics and provide a potential means to control product distribution.

To look at electron solvation with higher time resolution, we used low-viscosity pyrrolidinium salts and developed novel ionic liquids with even lower melting points and viscosities, based on ether-substituted pyrrolidinium cations. These liquids have RT viscosities low enough (65-95 cP) to flow through the picosecond pulse-probe transient absorption system at LEAF, which requires sample exchange to avoid cumulative radiation effects. Consequently, the electron solvation process was directly observed in three ILs by monitoring the decay of pre-solvated electrons at multiple wavelengths (to yield a solvated electron spectrum similar to the blue curve above). In *N*-methyl,*N*-butyl-pyrrolidinium NTf₂⁻ the electron solvation lifetime $\langle\tau_{\text{solv}}\rangle$ is 260 ps, while $\langle\tau_{\text{solv}}\rangle$ obtained from coumarin 153 Stokes shift measurements is 346 ps (see next section).

Even slower solvation processes were observed in pulse radiolysis studies of ionic liquids containing ether-, alcohol- and alkyl-functionalized quaternary ammonium dications $(\text{CH}_3)_2(\text{R})\text{N}^+(\text{CH}_2)_n\text{N}^+(\text{R})(\text{CH}_3)_2$ (NTf₂⁻)₂, where R = (CH₂)₃OH, (CH₂)₂OCH₂CH₃, or (CH₂)₃CH₃ and n = 3–8. Spectra on nanosecond timescales revealed that solvation of the excess electron is particularly slow in the case of the alcohol-derivatized ionic liquids. The blue shift of the electron spectrum to the customary 650 nm peak takes 25-40 nanoseconds at RT (viscosities ~4500-6800 cP). Comparison with the ~1 ns electron solvation time observed in similarly viscous 1,2,6-trihydroxyhexane (2500 cP) reveals the hindering effect of the ionic liquid lattice on hydroxypropyl side chain reorientation [1].

Solvation dynamics in ILs using fluorescent probes. The solvation and reorientational dynamics for a series of four ionic liquids were probed as functions of temperature (278-353 K) using coumarin 153 (C153). The ionic liquids are comprised of saturated organic cations (methyltributylammonium, hexyltributylammonium, methylbutylpyrrolidinium, and methyl(ethoxyethyl)pyrrolidinium) paired with a common anion, bis(trifluoromethylsulfonyl)imide. The observed solvation dynamics and fluorescence depolarization dynamics occur over a broad range of time scales that can only be adequately fit by functions including three or more exponential components. Stretched exponential distributions could not adequately fit our data. For both the solvation dynamics and the probe reorientational dynamics, the observed temperature dependences of the average relaxation times are well fit by Vogel-Tammann-Fulcher laws. To correlate the observed microscopic dynamics with macroscopic physical properties, temperature-dependent viscosities were also measured. Differential scanning calorimetry was used to study the thermodynamics of the phase transitions from the liquid to supercooled liquid to glassy states. For the two tetraalkylammonium liquids, the observed melting transitions occur near 300 K, so we are able to study the dynamics in a clearly supercooled regime. [10] (In collaboration with E. W. Castner, Rutgers University.)

EPR studies of radical species in ILs. Since our standard technique of transient optical detection cannot detect many important intermediates that lack strong absorption features, particularly hole-derived species, we have begun to use EPR to identify ionization products in ILs [11]. Radical intermediates were generated by radiolysis or photoionization of low-temperature ionic liquid glasses composed of ammonium, phosphonium, pyrrolidinium, and imidazolium cations and bis(triflyl)amide, dicyanamide, and bis(oxalato)borate anions. Large yields of terminal and penultimate C-centered radicals are observed in the aliphatic chains of the phosphonium, ammonium and pyrrolidinium cations, but not for imidazolium cation (where the ring is the predominant site of oxidation). This pattern is indicative of efficient deprotonation of a hole trapped on the parent cation (the radical dication) that competes with rapid electron transfer from a nearby anion. This charge transfer leads to the formation of stable N- or O-centered radicals; the dissociation of parent anions is a minor pathway. Production of •CF₃ from (CF₃SO₂)₂N⁻ evidently proceeds primarily through an excited state of the anion rather than via ionization.

Radiolysis of simulated IL-based nuclear extraction systems. Addition of 10-40 wt% of trialkylphosphate (a common agent for nuclear separations) has relatively little effect on the fragmentation of the ILs. The yield of the alkyl radical fragment generated by dissociative electron attachment to the trialkylphosphate is < 4% of the yield of the radical fragments derived from the IL solvent. The currently used hydrocarbon/tributylphosphate extraction systems involve a highly resistant, structurally simple solvent (like kerosene) that efficiently transfers charge and energy to the functional solute (tributylphosphate), resulting in the fragmentation of the latter and degradation of extraction efficiency. The results suggest a different paradigm for radiation protection: a solvent in which the

damage transfer is reversed. Such a solvent actively protects the functional solute in a sacrificial way, but overall radiolytic damage is still kept to a low level by the radiolytic properties of the solvent [11] (in collaboration with I. Shkrob and S. Chemerisov, ANL).

Radiolysis of borated ionic liquids. A group from Los Alamos calculated that processing plutonium in boron-containing ionic liquids could substantially reduce the risk of nuclear criticality accidents. Subsequently we investigated the radiation chemistry of ionic liquids prepared from carborane (CB^-) and bis(oxalato)borate (BOB^-) anions. Experiments in liquids derived from the $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ and BOB^- anions and studies of the same anions diluted in NTf_2^- ionic liquids indicate the major radiation stability concern may be the reaction of the solvated electron with the CB and BOB anions, a problem that could be addressed by including imidazolium or pyridinium cations in the ionic liquid mixtures. By contrast, trialkylammonio borate anions ($[\text{R}_3\text{N}-\text{B}_{12}\text{H}_{11}]^-$) form low-melting salts with many cations but do not react with solvated electrons (with D. Gabel, Bremen, submitted).

Future Plans

Electron solvation and reactivity. Pre-solvated electron scavenging mechanisms will be explored by studying the competition between the electron solvation and attachment processes in ILs. Electron solvation dynamics in several families of low-viscosity ILs will be measured by pulse-probe radiolysis. Subsequently, scavengers will be added to measure the kinetics of pre-solvated electron capture. It is well known from work in molecular solvents that many scavengers, for example SeO_4^{2-} , have widely different reactivity profiles towards pre-solvated and solvated electrons. We have begun quantitative measurement of the scavenging profiles of benzophenone, SeO_4^{2-} , NO_3^- , and Cd^{2+} using the ultrafast single-shot detection system at LEAF, through which we hope to explain such conundrums mechanistically. C-153 solvation dynamics results will be compared with electron and benzophenone anion solvation measurements.

Charge transport in ionic liquids. ILs have proved to possess valuable characteristics for solar energy photoconversion systems such as the Grätzel cell. Pulse radiolysis and flash photolysis methods will be used to study how ionic liquids affect charge-transport reactions in bridged electron donor-acceptor systems. Focus areas will be the combined effects of ionic solvation and slow solvent relaxation on the energy landscape of charge transport, including specific counterion effects depending on the ionic liquid, and the influence of the lattice-like structure of ionic liquids on the distance dependence of electron transport reactions.

Non-classical diffusion in ionic liquids. Ionic liquids show unusual solute diffusion behavior on the basis of solute charge and size, which will be explored through reaction kinetics and high-pressure pulsed-gradient spin echo NMR studies of diffusion rates of charged and neutral species. This information is important for modeling geminate recombination kinetics to understand why radiolytic damage accumulates slower in ionic liquids than many other materials.

EXAFS studies of structure and reaction dynamics in ionic liquids. In collaboration with R. Crowell and coworkers, we will use Br EXAFS to study the structures of neat bromide ionic liquids and the effect of solutes, and we will use photoionization coupled with time-resolved EXAFS to probe the solvation dynamics of Br^0 atoms in ILs and the effect of the ionic liquid environment on the $\text{Br}^- + \text{Br}^0 \rightarrow \text{Br}_2^-$ reaction. The results can be applied to understanding related iodide systems of interest in solar photoconversion.

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